

The invention claimed is:

1. A process for the production of dialkyl carbonate comprising the steps of:
 - (a) feeding a stream comprising urea, alcohol, water and ammonium carbamate to a first reaction zone:
 - (b) concurrently in said first reaction zone,
 - (i) reacting water with urea to form ammonium carbamate,
 - (ii) decomposing ammonium carbamate into ammonia and carbon dioxide, and
 - (c) removing ammonia, carbon dioxide and alcohol from said first reaction zone;
 - (d) removing urea and alcohol from said first reaction zone;
 - (e) feeding said urea and alcohol to a second reaction zone;
 - (f) reacting alcohol and urea in the presence of a homogeneous catalyst comprising an organotin complex compound of dialkylalkoxide in a high boiling solvent to form dialkyl carbonate and
 - (g) removing dialkyl carbonate and alcohol from said second reaction zone.
2. The process according to claim 1 wherein alcohol and urea react to form alky carbamate in said first reaction zone.
3. The process according to claim 1 wherein said alcohol is a C₁-C₃ alcohol.
4. The process according to claim 1 comprising:
 - (a) feeding said stream containing urea, methanol, water and ammonium carbamate to a first reaction zone:
 - (b) concurrently in said first reaction/distillation zone,
 - (i) reacting water with urea to form ammonium carbamate,
 - (ii) decomposing the ammonium carbamate in the feed and the ammonium carbamate from the reaction of water with urea into ammonia and carbon dioxide, and

(iii) separating the ammonia, carbon monoxide and methanol from the urea and by distillation;

(c) removing ammonia, carbon dioxide and methanol from said first reaction/distillation zone as a first overheads;

(d) removing urea and methanol from said first reaction/distillation zone as a first bottoms;

(e) feeding said first bottoms and methanol to a second reaction/distillation zone;

(f) concurrently in said second reaction/distillation zone,

(i) reacting methanol and urea in the presence of a homogeneous catalyst comprising an organotin complex compound of dialkylmethoxide in a high boiling solvent to form dimethyl carbonate and

(ii) separating dimethyl carbonate and ammonia from the homogeneous catalyst by distillation.

(g) removing dimethyl carbonate and methanol from said second reaction/distillation zone as a second overheads; and

(h) removing a second bottoms from said second distillation column reactor.

5. The process according to claim 4 wherein the dimethyl carbonate in said second overheads is separated from the methanol by extractive distillation.

6. The process according to claim 4 wherein an inert diluent is added to said first overheads.

7. The process according to claim 4 wherein the methanol in said first overheads is condensed and a portion of said condensed methanol is returned to near the top of said first distillation column reactor as reflux and the remainder of said condensed methanol is returned to the lower section of said first distillation column reactor.

8. The process according to claim 4 wherein a first portion of said second bottoms is fed to said first distillation column reactor, a second portion of said second

bottoms is recycled to said second distillation column and a third portion of said second bottoms is fed to a third distillation column reactor for catalyst regeneration and heavies cleanup.

9. The process according to claim 4 wherein said second overheads is condensed and a portion of said condensed second overheads is returned to said second distillation column reactor as reflux.

10. A process for the production of dimethyl carbonate comprising the steps of:

(a) feeding a stream containing urea, methanol, water and ammonium carbamate to a first distillation column reactor:

(b) concurrently in said first distillation column reactor,

(i) reacting a portion of said urea with a portion of said methanol to produce methyl carbamate,

(ii) reacting water with urea to form ammonium carbamate,

(iii) decomposing the ammonium carbamate in the feed and the ammonium carbamate from the reaction of water with urea into ammonia and carbon dioxide, and

(iv) separating the ammonia, carbon monoxide and methanol from the urea and methyl carbamate by distillation;

(c) removing ammonia, carbon dioxide and methanol from said first distillation column reactor as a first overheads;

(d) removing urea and methyl carbamate from said distillation column reactor as a first bottoms;

(e) feeding said first bottoms and methanol to a second distillation column reactor;

(f) concurrently in said second distillation column reactor,

(i) reacting methanol and urea in the presence of a homogeneous catalyst comprising an organotin complex compound of dialkylmethoxide in a high boiling solvent to form dimethyl carbonate and

(ii) separating dimethyl carbonate and ammonia from the homogeneous catalyst by distillation;

(g) removing dimethyl carbonate and methanol from said second distillation column reactor as a second overheads;

(h) removing homogeneous catalyst from said second distillation column reactor as a second bottoms;

(i) separating the dimethyl carbonate from the methanol in said second overheads by extractive distillation; and

(j) feeding a first portion of said second bottoms to said first distillation column reactor;

(k) feeding a second portion of said second bottoms to a third distillation column reactor where the catalyst is regenerated and cleaned up of heavies; and

(l) recycling a third portion of said second bottoms to said second distillation column reactor.

11. in a process for the production of dialkyl carbonates by the reaction of reactants comprising urea and alcohol having water and ammonium carbonate as impurities comprising the steps of:

(a) feeding reactants comprising urea and alcohol to a primary reaction zone;

(b) feeding an organotin compound and a high boiling electron donor atom containing solvent to said primary reaction zone; and

(c) concurrently in said primary reaction zone

(i) reacting alcohol and urea in the presence of said organotin compound and said high boiling electron donor atom containing solvent to produce dialkyl carbonate; and

(ii) removing the dialkyl carbonate and ammonia from said primary reaction zone as vapor,

wherein the improvement is the use of a preliminary reaction zone before the primary reaction zone to remove water, and ammonium carbamate from said reactants, by feeding the reactants, first to the preliminary reaction zone under conditions to react said water with urea to form ammonium carbamate and decompose ammonium carbamate to ammonia and carbon dioxide and removing the

ammonia and carbon dioxide from said reactants prior to feeding the reactants in step (a).

12. The process according to claim 11 where the temperature of the preliminary reaction zone is at a temperature in the range from 200 to 380° F in liquid phase.

13. The process according to claim 12 where the temperature of the preliminary reaction zone is in the range of from 250 to 350° F.

14. The process according to claim 11 wherein a portion of the methanol feed reacts with a portion of the urea feed to form methyl carbamate in the preliminary reaction zone.

15. The process according to claim 11 wherein the preliminary reaction zone and primary reaction zone are operated under distillation conditions.

16. The process according to claim 11 wherein the water is removed from the feeds by reacting it with urea to form ammonium carbamate which in turn decomposes to ammonia and carbon dioxide.

17. The process according to claim 16 where the temperature of the preliminary reaction zone is at a temperature in the range from 200 to 380° F in liquid phase.

18. The process according to claim 11 wherein the ammonium carbamates are removed from the feeds by decomposition to ammonia and carbon dioxide.

19. The process according to claim 18 wherein the temperature of the preliminary reaction zone is at a temperature in the range from 200 to 380° F in liquid phase.

20. The process according to claim 11 wherein the said high boiling electron donor atom compound comprises triethylene glycol dimethyl ether.